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14. ABSTRACT

Invented a new technique for patterning — microdisplacement printing — that solves the pattern dissolution issues inherent in microcontact printing. Worked out the kinetics and mechanism of displacement. Modeled displacement and showed that displacement kinetics follow a universal form. Commercialized molecules used for displacement. Developed a special resist stack that improves line edge roughness and produces highly optimized parent structures for molecular rulers. This was previously the limitation of the technique. Investigated failure modes both quantitatively and microscopically, targeting and analyzing failures by type and with intelligent design of test structures to elucidate the contributions and origins of different failure modes. Automated molecular ruler deposition, greatly enhancing the precision of the process. Demonstrated sacrificial layers and generations using molecular-ruler nanolithography. Used sacrificial layers to create daughter and parent structures of equal height. This can also be used to eliminate Au from the processing for compatibility with semiconductor processing. Created a method for ultrahigh

15. SUBJECT TERMS

resolution nanoimprint masters using molecular rulers on quartz. Demonstrated an all self-assembly method of molecular-ruler nanolithography by creating parents with shadow sphere nanolithography.

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Final Report for DARPA/AFOSR Advanced Nanolithography Program

Chemically Advanced Nanolithography
DARPA/AFOSR #F49620-02-1-0386/BAA01-36

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June 2007

Objectives

Combine self- and directed assembly with nanolithographic methods to yield enhanced precision and capabilities in patterning at the nanoscale.

Overview

We have made tremendous gains in applying self-assembly to lithography. We have come up with new resist structures. We have invented new techniques for soft lithography that enhance pattern precision and prevent pattern dissolution. We have developed novel methods for chemical patterning using both soft lithography and hybrid methods. We have developed metrology tools for measuring these patterns. Our efforts have been transitioned in a number of areas.

Accomplishments/New Findings

1. Invented a new technique for patterning – microdisplacement printing – that solves the pattern dissolution issues inherent in microcontact printing. Worked out the kinetics and mechanism of displacement. Modeled displacement and showed that displacement kinetics follow a universal form. Commercialized molecules used for displacement.

2. Developed a special resist stack that improves line edge roughness and produces highly optimized parent structures for molecular rulers. This was previously the limitation of the technique.

3. Investigated failure modes both quantitatively and microscopically, targeting and analyzing failures by type and with intelligent design of test structures to elucidate the contributions and origins of different failure modes.

4. Automated molecular ruler deposition, greatly enhancing the precision of the process.

5. Demonstrated sacrificial layers and generations using molecular-ruler nanolithography.

6. Used sacrificial layers to create daughter and parent structures of equal height. This can also be used to eliminate Au from the processing for compatibility with semiconductor processing.

7. Created a method for ultrahigh resolution nanoimprint masters using molecular rulers on quartz.

8. Demonstrated an all self-assembly method of molecular-ruler nanolithography by creating parents with shadow sphere nanolithography.

9. Showed that control of exposed functionality in dip-pen nanolithography (prepositioned structures) plays an important role in pattern placement and precision.

10. Demonstrated the compatibility of molecular rulers with conventional (*i.e.*, photolithographic) processing before, during and after multilayer deposition, enabling molecular rulers to be used in semiconductor processing.

11. Invented a new technique for patterning – microcontact insertion printing – that places diluted single molecules in patterns.

Personnel Supported

Mary Anderson
Arrelaine Dameron
Julia Heetderks
J. Nathan Hohman
R. Jayaraman
Adam Kurland
Penelope Lewis (was on the faculty of Skidmore College, now at Columbia University)
Morgan Mihok
Jason Monnell (now on the research faculty of the University of Pittsburgh)
Amanda Moore
Thomas J. Mullen
Mathew Sandel
Rachel Smith
Charan Srinivasan
Jackie Tan

Dr. Luis C. Fernández-Torres (now on the faculty of the University of Puerto Rico at Cayey)
Dr. Susan Gillmor (now on the faculty of George Washington University)
Dr. Jennifer Hampton (now on the faculty of Hope College)
Dr. E. Charles H. Sykes (now on the faculty of Tufts University)
Dr. Hirofumi Tanaka (now at the Institute of Molecular Science)

Prof. Mark W. Horn
Prof. Haiwon Lee (now Vice President for Research at Hanyang University and on Korea's NNI Board)
Prof. Paul S. Weiss

Publications

1. *Exploiting Intermolecular Interactions and Self-Assembly for Ultrahigh Resolution Nanolithography*, M. E. Anderson, R. K. Smith, Z. J. Donhauser, A. Hatzor, P. A. Lewis, L. P. Tan, H. Tanaka, M. W. Horn, and P. S. Weiss, *Journal of Vacuum Science and Technology B* **20**, 2739 (2002). Also appeared in the *Virtual Journal of Nanoscale Science and Technology*.

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3. *Nanofabrication Using Self-Assembled Monolayers -- Precise Nanolithography Using Intermolecular Interactions and Self-Assembly*, H. Tanaka, M. E. Anderson, R. K. Smith, Z. J. Donhauser, A. Hatzor, P. A. Lewis, L. P. Tan, M. W. Horn, and P. S. Weiss, *Japanese Society of Applied Physics: Thin Film and Surface Physics Division* **118**, 10 (2003).

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8. *Super-Precise Nanolithography Using Multilayers of Self-Assembled Monolayers*, H. Tanaka, M. E. Anderson, L.-P. Tan, M. Mihok, M. W. Horn, and P. S. Weiss, *Journal of the Surface Science Society of Japan* **25**, 650 (2004).

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10. *Utilizing Self-Assembled Multilayers in Lithographic Processing for Nanostructure Fabrication: Initial Evaluation of the Electrical Integrity of Nanogaps*, M. E. Anderson, C. Srinivasan, R. Jayaraman, P. S. Weiss, and M. W. Horn, *MicroElectronic Engineering* **78-79**, 248 (2005).

11. *Structures and the Displacement of 1-Adamantanethiol Self-Assembled Monolayers on Au{111}*, A. A. Dameron, L. F. Charles, and P. S. Weiss, *Journal of the American Chemical Society* **127**, 8697 (2005).

12. *Microdisplacement Printing*, A. A. Dameron, J. R. Hampton, R. K. Smith, T. J. Mullen, S. D. Gillmor, and P. S. Weiss, *Nano Letters* **5**, 1834 (2005).

13. *Enhanced Molecular Patterning via Microdisplacement Printing*, A. A. Dameron, J. R. Hampton, S. D. Gillmor, J. N. Hohman, and P. S. Weiss, *Journal of Vacuum Science and Technology B* **23**, 2929 (2005).

14. *Transport Rates Vary with Deposition Time in Dip-Pen Nanolithography*, J. R. Hampton, A. A. Dameron, and P. S. Weiss, *Journal of Physical Chemistry B* **109**, 23118 (2005).

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18. *Photolithographic Structures with Precise Controllable Nanometer-Scale Spacings Created by Molecular Rulers*, M. E. Anderson, L. P. Tan, M. Mihok, H. Tanaka, M. W. Horn, G. S. McCarty, and P. S. Weiss, *Advanced Materials* **18**, 1020 (2006).

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23. *Extensions of Molecular Ruler Technology for Nanoscale Patterning*, C. Srinivasan, M. E. Anderson, E. M. Carter, J. N. Hohman, S. S. N Bharathwaja, S. Trolier-Mckinstry, P. S. Weiss, and Mark Horn, *Journal of Vacuum Science and Technology B* **24**, 3200 (2006).

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28. *Arrays of Cu^{2+}-Complexed Organic Clusters Grown on Gold Nano Dots*, A. Hatzor de Picciotto, A. D. Wissner-Gross, G. Lavallee, and P. S. Weiss, *Journal of Experimental Nanoscience* **2**, 3 (2007).

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31. *Dynamics of Solution Displacement in 1-Adamantanethiolate Self-Assembled Monolayers*, T. J. Mullen, A. A. Dameron, H. M. Saavedra, M. E. Williams, and P. S. Weiss, *Journal of Physical Chemistry C* **111**, 6740 (2007).

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33. *Designing, Measuring and Controlling Molecular- and Supramolecular-Scale Properties for Molecular Devices*, P. S. Weiss, in *Proceedings of Polymer Materials, Science, and Engineering (American Chemical Society, Division of Polymer Materials Science and Engineering)* (2007), in press.

34. *Molecular Devices*, A. M. Moore, D. L. Allara, and P. S. Weiss, in *NNIN Nanotechnology Open Textbook* (2007), in press.

35. *1-Adamantanethiolate Monolayer Displacement Kinetics Follow a Universal Form*, H. M. Saavedra, C. M. Barbu, A. A. Dameron, T. J. Mullen, V. H. Crespi, and P. S. Weiss, submitted for publication.

36. *Nanostructures Using Self-Assembled Multilayers as Molecular Rulers and Etch Resists*, C. Srinivasan, J. N. Hohman, M. E. Anderson, P. S. Weiss, and M. W. Horn, submitted for publication.

37. *Nanoscale Patterning on Quartz*, C. Srinivasan, J. N. Hohman, M. E. Anderson, P. S. Weiss, and M. W. Horn, submitted for publication.

38. *Scanning Electron Microscopy Metrology for Enhanced Chemical Patterning Methods*, C. Srinivasan, T. J. Mullen, M. E. Anderson, A. A. Dameron, A. M. Andrews, E. C. Dickey, M. W. Horn, and P. S. Weiss, submitted for publication.

Interactions/Transitions

A. Presentations and Workshops

We held a NanoApplications Workshop, co-sponsored with the Center for Innovative Management at North Carolina State University on brainstorming applications for molecular rulers. Attendees included scientists, managers, and investors from IBM, Bayer, Adams Capital Management, and elsewhere.

We described our methods at an NNIN workshop on hybrid nanolithographies at Harvard University.

We presented our work at the industrial forum NSTI meeting, and at Semiconductor Research Corporation Workshops.

We have supplied the national area expertise in this area to the National Nanotechnology Infrastructure Network, including two staff members (and a third is about to be signed).

We gave many invited and plenary lectures on this work.

B. Consultative/Advisory

GeoCenters Technical Advisory Board.
RHK Scientific Advisory Board.
SAIC Technical Advisory Board.
Zyvex Scientific Advisory Board.

C. Transitions

IBM reproduced our molecular rulers automation set-up. They borrowed one of our students for a summer and then another month the following year to help them set up this apparatus. We have exchanged multiple visits.

Sigma-Aldrich has begun to manufacture 1-adamantanethiol. They sent us a sample to verify that theirs was useful for microdisplacement printing. We published a Technical Application Note on how to use it. We now have an agreement through which Sigma will synthesize (and commercialize) molecules useful for patterning. These will be designed and optimized collaboratively. The PI will visit them later this month to further this collaboration. The CEO of Sigma and the Head of the Materials Division have visited several times.

Veeco had us test and improve their dip-pen nanolithography software. We used the enhanced software in two publications. The changes we made have been commercialized and they are asking for continued collaborations in this area.

We have given a number of presentations to and for the Semiconductor Research Corporation and have received funding for these efforts. We have had direct connections for this work with AMD, IBM, Intel, Semiconductor Research Corporation, and Texas Instruments.

New Discoveries

We invented a new means to create ultrahigh resolution masters for nanoimprint lithography.

We invented microdisplacement printing.

We invented microcontact insertion printing.

We invented a hybrid photolithographic strategy for chemical patterning.

We discovered that we could use sacrificial generations in molecular rulers to create nanostructures.

We discovered a means to create devices that are already connected by virtue of their fabrication.

Honors/Awards

Paul Weiss was named Distinguished Professor of Chemistry and Physics, 2005.
Paul Weiss was named Nanofabrication Faculty Fellow, 2005.
Paul Weiss was named Senior Editor of *IEEE Electron Device Letters*, 2005.
Paul Weiss gave the Eminent Scholar Lecture at the University of Arizona, 2006.
Paul Weiss gave the Levine Lectures at the University of Pittsburgh, 2007.
Paul Weiss was named Founding Editor-in-Chief of *ACS Nano*.
Beth Anderson won the Apple Fellowship, 2004.
Beth Anderson won a National Research Council Fellowship, 2006 (declined).
Arrelaine Dameron won the Weyenberg Award, 2005.
Arrelaine Dameron won the Rustum and Della Roy Innovation in Materials Research Award, 2006.
Amanda Moore won the Apple Fellowship and the Geiger Fellowship, 2006.
Amanda Moore won the Rohm & Haas Graduate Student Award, 2007.
Amanda Moore won the national Iota Sigma Pi Anna Louise Hoffman Award for Outstanding Achievement in Graduate Research, 2007.
TJ Mullen won the Rohm & Haas Graduate Student Award, 2006
TJ Mullen won the Braucher Award and the Geiger Fellowship, 2006.
TJ Mullen won the Rustum and Della Roy Innovation in Materials Research Award, 2007.
TJ Mullen won the American Chemical Society, Division of Analytical Chemistry Fellowship sponsored by the Society of Analytical Chemists of Pittsburgh.